

## Interference of inorganic ions on phenol degradation by the Fenton reaction

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**ABSTRACT:** The addition of  $\text{Cu}^{2+}$  ions to the classical Fenton reaction ( $\text{Fe}^{2+}$  plus  $\text{H}_2\text{O}_2$  at pH 3) is found to accelerate the degradation of organic compounds. This synergic effect causes an approximately 15 % additional reduction of the total organic carbon (TOC), representing an overall improvement of the efficiency of the mineralization of phenol. Although  $\text{Fe}^{2+}$  exhibits a high initial rate of degradation, the degradation is not complete due to the formation of compounds refractory to the hydroxyl radical. The interference of copper ions on the degradation of phenol by the Fenton reaction was investigated. In the presence of  $\text{Cu}^{2+}$ , the degradation is slower, but results in a greater reduction of TOC at the end of the reaction ( $t = 120$  min). In the final stages of the reaction, when the  $\text{Fe}^{3+}$  in the solution is complexed in the form of ferrioxalate, the copper ions assume the role of the main catalyst of the degradation.

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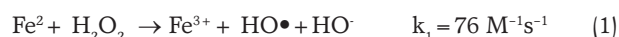
### Introduction

Currently, there is great concern with the environment, particularly regarding the pollution of water resources, leading to a search for technologies to treat domestic and industrial waste. Among these new technologies, advanced oxidation processes (AOP) are potentially the most promising due to their high efficiency and versatility. Thus, a variety of classes of compounds can be completely mineralized by existing AOP, including compounds refractory to conventional biological treatment processes (Kiwi et al., 2000; Pérez et al., 2002; Pignatello et al., 2006).

The AOP are typically based on the generation of highly oxidizing species such as the hydroxyl radical ( $\text{HO}\cdot$ ), which has a high oxidation potential ( $E^\circ = +2.80$  V vs. NHE) and is capable of initiating reactions that can often lead to the total degradation of organic matter. Among the AOP, the Fenton reaction is perhaps the most promising as an alternative method for wastewater treatment due to its high oxidative power, very fast reaction rate, relatively low cost and ease of operation and maintenance (Walling and Camaioni, 1975).

The classic mechanism of the Fenton reaction is a simple redox reaction in which  $\text{Fe}^{2+}$  ions are oxidized

to  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  is reduced to a hydroxyl radical and hydroxide ion (Equation 1).



Copper also acts as a catalyst in the decomposition of  $\text{H}_2\text{O}_2$  (cupro-Fenton reaction), similar to iron (Aguiar et al., 2007). Both transition metals react with  $\text{H}_2\text{O}_2$  to form intermediate complexes that then decompose, forming the radical  $\text{HO}\cdot$ . Organic peroxides ( $\text{RO}_2\text{H}$ ) are decomposed by these metals to form alkoxyl radicals ( $\text{RO}\cdot$ ) and organic peroxy radicals ( $\text{RO}_2\cdot$ ). In the cupro-Fenton reaction, the complex formed between  $\text{H}_2\text{O}_2$  and the metal ion has been reported to be more stable than the analogous complex in the ferrous Fenton reaction (Johnson et al., 1985).

The oxidizing activity of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions has been evaluated for various phenolic compounds, mainly derivatives of catechol. Catechol is oxidized by  $\text{Cu}^{2+}$ , generating a semiquinone that is subsequently oxidized to form a quinone. Molecular oxygen ( $\text{O}_2$ ) can also act as the electron acceptor, being reduced by the semiquinone radical to superoxide/hydroperoxide,  $\text{O}_2\cdot^-/\text{HO}_2\cdot$ , which can be converted into  $\text{H}_2\text{O}_2$ . The mechanism proposed by Aguiar et al. (2007) for the reduction of  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  by catechol is outlined in Figure 1. Therefore, there are sev-

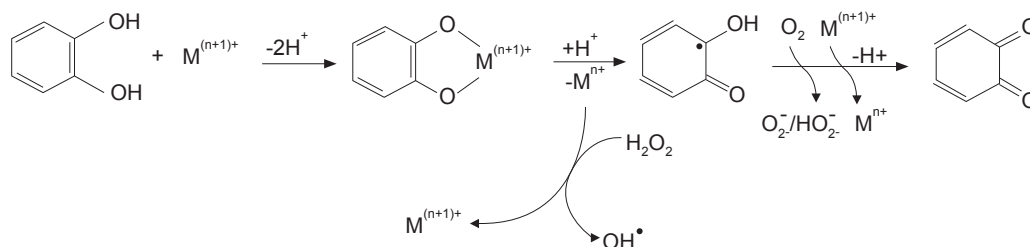


Figure 1 – Catechol oxidation by  $\text{Cu}^{2+}$  and formation of  $\text{HO}\cdot$  as proposed by Aguiar et al. (2007).

eral pathways involving phenolic compounds and metal ions that can potentially increase the efficiency of the Fenton process (Hamilton et al., 1966; Chen and Pignatello, 1997).

In this study, we report an investigation of the interference of copper ions on the degradation of phenol by the Fenton reaction.

## Materials and Methods

The following reagents were used: Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , Synth), copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , Synth), sodium sulfate ( $\text{Na}_2\text{SO}_4$ , Vetec), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 %, Synth), sulfuric acid ( $\text{H}_2\text{SO}_4$ , Synth), sodium hydroxide ( $\text{NaOH}$ , Merck), phenol (Aldrich), catechol (Acros), acetic acid (Merck), formic acid (Aldrich), oxalic acid (Aldrich) and acetonitrile (JT Baker), all reagent grade or superior, were used as received.

The solutions of phenol were prepared by directly dissolving the desired amount of phenol in aqueous solution. The reactor used for the degradation of phenol was a batch reactor with an internal volume of 1.0 L (Figure 2), protected from incident light in order to minimize the effect of photochemical reactions. The solution temperature was controlled at 30 °C using a thermostatic bath and magnetic stirring.

Initially, a solution containing 10 mM phenol, 0.5 mM  $\text{Fe}^{2+}$  and different concentrations of  $\text{Cu}^{2+}$  at pH = 3.0 was added to the reactor. Aqueous hydrogen peroxide was added slowly ( $3.33 \text{ mM min}^{-1}$ ), with the aid of a peristaltic pump, during the first 60 minutes of reaction to minimize the formation of the hydroperoxyl radical (Equation 2) (Kang et al., 2002).

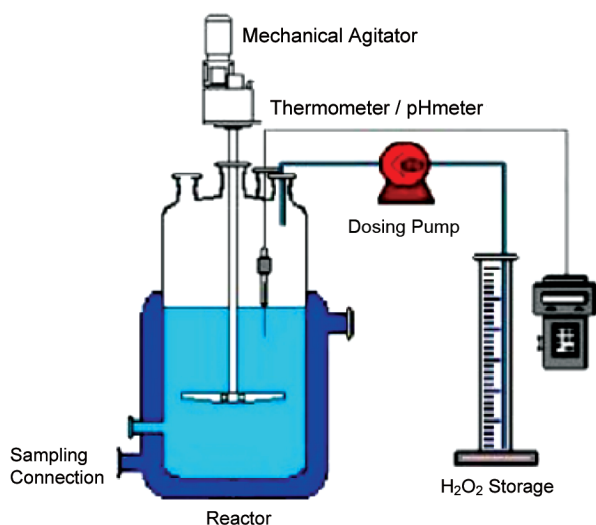


Figure 2 – Scheme of the reactor used for the degradation of phenol.

At selected time intervals, 5 mL of sample solution were collected and 2 drops of a solution of 2.0 M  $\text{NaOH}$  immediately added, raising the pH to  $\sim 12$ . The increase in pH precipitated  $\text{Fe}^{3+}$ , stopping the reaction. After filtration, the sample was reacidified to a pH around 3.0 to maintain the same conditions as in the reactor and total organic carbon (TOC) was analyzed with a Shimadzu Model TOC-5000A analyzer.

Phenol and the main degradation products (hydroxyaromatics and aliphatic acids) were identified and quantified by high performance liquid chromatography (for hydroxyaromatics - Shimadzu 2010A LC-MS, and for aliphatic acids - Shimadzu 20AD HPLC) using standard compounds for identification and calibration. For the determination of the aromatic intermediates, a Shim-pack C18 reverse phase column ( $5 \mu\text{m}$ ,  $4.6 \times 150 \text{ mm}$ ) was used with detection at 270 nm. The mobile phase consisted of an aqueous solution containing 0.2 % acetic acid (A) and acetonitrile containing 0.2 % acetic acid (B). During 3 min, the mobile phase (flow rate  $0.7 \text{ mL min}^{-1}$ ) was 18 % B: 82 % A, followed by a gradient of 18-58 % B over 10 min and completing the analysis by reverting for 1 min to 18 % B: 82 % A. To determine the intermediate acids, a Hamilton PRP brand-X300 ion exchange column was used with detection at 220 nm. The mobile phase consisted of an aqueous solution of  $\text{H}_2\text{SO}_4$  (pH  $2.00 \pm 0.02$ ), at a flow rate of  $1 \text{ mL min}^{-1}$ , with the column temperature maintained at 30 °C. Before being injected onto the ion exchange column, the samples were filtered through a C18 cartridge previously activated with methanol. This step removed the remaining aromatic compounds, necessary since these compounds are strongly retained on the ion exchange column, resulting in broad bands that hamper analysis (Machuleck et al., 2007).

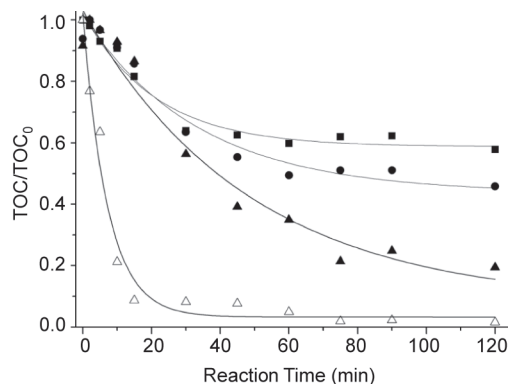


Figure 3 – Effect of added ions on the degradation of phenol during the Fenton reaction. Experimental conditions:  $[\text{phenol}]_{\text{initial}} = 10 \text{ mM}$ ;  $[\text{Fe}^{2+}] = 0.5 \text{ mM}$ ;  $[\text{H}_2\text{O}_2] = 200 \text{ mM}$ ;  $\text{pH}_{\text{initial}} = 3.0$ ; absence of added  $\text{Cu}^{2+}$  (■);  $1.0 \text{ mM Cu}^{2+}$  (●);  $2.0 \text{ mM Cu}^{2+}$  (▲) or  $50 \text{ mM Cu}^{2+}$  (Δ).

## Results and Discussion

The addition of  $\text{Cu}^{2+}$  affected the rate of oxidation of phenol ( $p < 0.051$ ), and an increase in the concentration of  $\text{Cu}^{2+}$  increased the rate of reaction (Figure 3). In the presence of only  $\text{Fe}^{2+}$  (Fenton reaction), the net decrease of the TOC is only 40 % after 120 min. However, upon addition of sufficient  $\text{Cu}^{2+}$  ( $\geq 5.0$  mM) to the Fenton reaction, the degradation is almost complete by 60 min, implicated in the reduction of organic material, enhancing the degradation of the pollutant, in this case the phenol.

Figure 4 further illustrates the synergy between  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  in the degradation of phenol (TOC reduction). Thus, little or no mineralization is observed in the presence of 0.50 mM  $\text{Cu}^{2+}$  alone. In the presence of  $\text{Fe}^{2+}$  ion alone, the mineralization reaches a maximum of ca. 40-45 % after 30 minutes of reaction. Combining the two ions, in a cupro-Fenton reaction, the mineralization reaches 60 % at the end of the reaction. It was initially analyzed the concentration of phenol as a function of reaction time (Figure 5). Phenol was completely degraded in 15 min in both the Fenton and cupro-Fenton reactions, but only at a much slower rate by  $\text{Cu}^{2+}$  alone in the absence of  $\text{Fe}^{2+}$ .

The two intermediates initially formed in the degradation of phenol are catechol and hydroquinone, both of which can act as catalysts for the Fenton (Zanta et al., 2010) and cupro-Fenton reactions (Valenzuela et al., 2008) due to the regeneration of  $\text{Fe}^{2+}$  and  $\text{Cu}^{1+}$ . In the presence of  $\text{Cu}^{2+}$ , the amount of catechol generated was much lower (Figure 6), explaining the much lower catalytic effect on phenol degradation (Figure 5).

The analysis of the organic compounds remaining at the end of the reaction showed the formation of oxalic acid (OA) (Figure 7) and formic acid (FA) (Figure 8). OA is not degraded in the Fenton reaction due to formation of the ferrioxalate complex, which removes free iron from the solution and stops the reaction. Acetic acid was also detected, but it was quickly oxidized to  $\text{CO}_2$  and water. Oxalic acid and formic acid proved to be the two most refractory intermediates and could be detected up until the end of the reaction, in agreement with other authors (Kwon et al., 1999). In the presence of  $\text{H}_2\text{O}_2$ ,  $\text{Cu}^{2+}$  is regenerated by the Fenton reaction between  $\text{Cu}^{1+}$  and  $\text{H}_2\text{O}_2$  (Equation 3) under experimental conditions in which  $\text{HO}^\bullet$  radicals are formed.

The study of the primary reactions of the thermal step of the Fenton reaction in the presence of copper ions suggests the possible role of copper ions. Catechol and/or hydroquinone formed by the Fenton oxidation of phenol can reduce  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  (Figure 1). The reaction of copper (I) ions with  $\text{H}_2\text{O}_2$  can regenerate  $\text{Cu}^{2+}$  via a reaction similar to the Fenton reaction, forming  $\text{HO}^\bullet$  radicals (Equation 3).

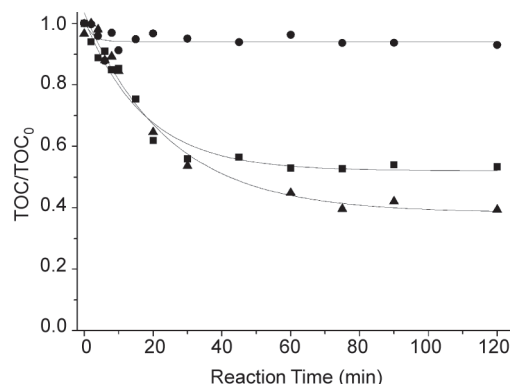
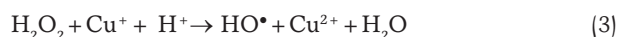


Figure 4 – Effect of added  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  ions on the degradation of phenol. Experimental conditions:  $[\text{phenol}]_{\text{initial}} = 10$  mM;  $[\text{H}_2\text{O}_2] = 200$  mM;  $\text{pH}_{\text{initial}} = 3.0$ ; 0.50 mM  $\text{Cu}^{2+}$  (●); 0.50 mM  $\text{Fe}^{2+}$  (■) or 0.50 mM  $\text{Fe}^{2+}$  + 0.50 mM  $\text{Cu}^{2+}$  (▲).

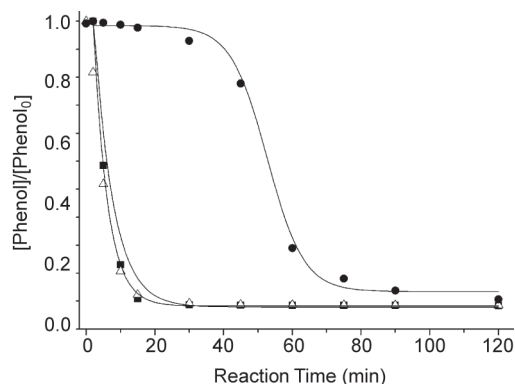


Figure 5 – Variation of the concentrations of phenol with time. Effect of inorganic ions on the degradation of 10 mM phenol.  $[\text{H}_2\text{O}_2] = 200$  mM,  $\text{pH}_{\text{initial}} = 3.0$  and  $T = 30$  °C; 0.50 mM  $\text{Cu}^{2+}$  (●), 0.50 mM  $\text{Fe}^{2+}$  (■) or 0.50 mM  $\text{Fe}^{2+}$  + 0.50 mM  $\text{Cu}^{2+}$  (Δ).

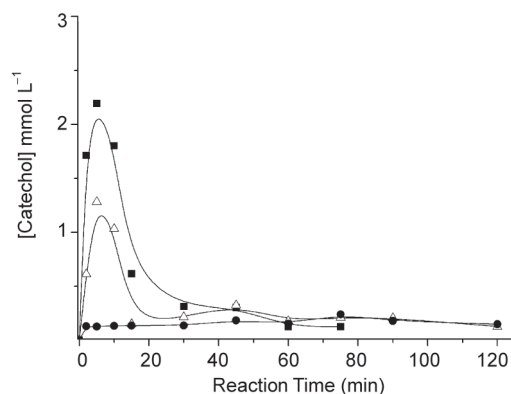


Figure 6 – Variation of the concentration of catechol with the time during the degradation of 10 mM phenol in the presence of inorganic ions.  $[\text{H}_2\text{O}_2] = 200$  mM,  $\text{pH}_{\text{initial}} = 3.0$  and  $T = 30$  °C; 0.50 mM  $\text{Cu}^{2+}$  (●), 0.50 mM  $\text{Fe}^{2+}$  (■) or 0.50 mM  $\text{Fe}^{2+}$  + 0.50 mM  $\text{Cu}^{2+}$  (Δ).

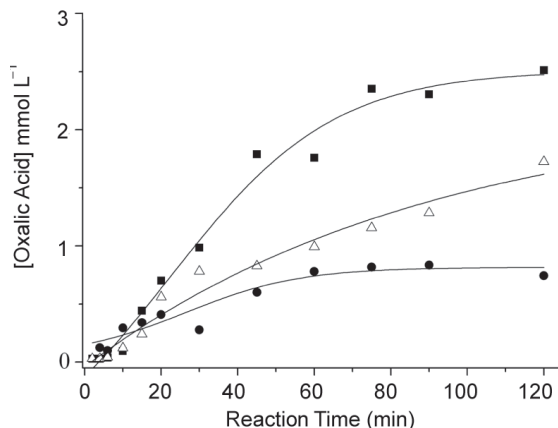


Figure 7 – Variation of the concentrations of oxalic acid with the time during the degradation of 10 mM phenol in the presence of inorganic ions.  $[H_2O_2] = 200$  mM,  $pH_{initial} = 3.0$  and  $T = 30$  °C; 0.50 mM  $Cu^{2+}$  (●), 0.50 mM  $Fe^{2+}$  (■) or 0.50 mM  $Fe^{2+} + 0.50$  mM  $Cu^{2+}$  (Δ).

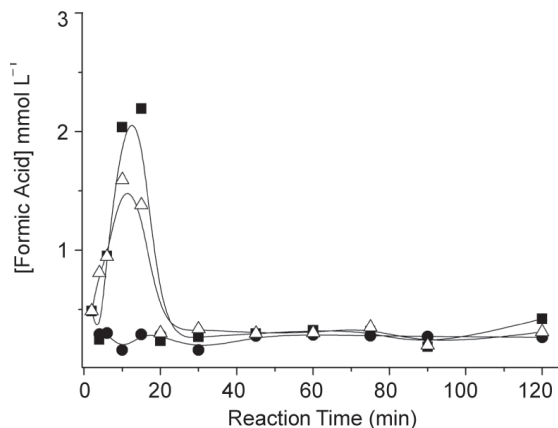
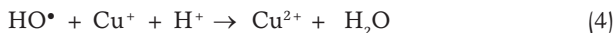


Figure 8 – Variation of the concentrations of formic acid with the time during the degradation of 10 mM phenol in the presence of inorganic ions.  $[H_2O_2] = 200$  mM,  $pH_{initial} = 3.0$  and  $T = 30$  °C; 0.50 mM  $Cu^{2+}$  (●), 0.50 mM  $Fe^{2+}$  (■) or 0.50 mM  $Fe^{2+} + 0.50$  mM  $Cu^{2+}$  (Δ).

These  $HO^\bullet$  radicals can oxidize  $Cu^{1+}$  to form  $Cu^{2+}$  (Equation 4) or, in the presence of excess  $H_2O_2$ , be consumed by another molecule of  $H_2O_2$  to produce  $HOO^\bullet$  and  $O_2^\bullet$  (Equation 5) (Liu et al., 2005).



In the final stages of the reaction, when iron is complexed in the form of ferrioxalate, copper ions continue to degrade intermediates in the oxidation process, resulting an increase in the overall mineralization of phenol.

## Conclusions

In the conventional Fenton reaction with  $Fe^{2+}/Fe^{3+}$  and  $H_2O_2$ , aliphatic organic acids formed in the degradation of phenol (mainly oxalic acid) make it difficult to obtain complete mineralization, resulting in a final TOC value that is quite high. The combination of the Fenton reaction with a cupro-Fenton reaction can increase the overall efficiency of the process, a synergistic effect that occurs mainly in the final stages of the degradation and mineralization.

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